Coherent bimolecular reactions with quantum-degenerate matter waves

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We demonstrate theoretically that the abstraction reaction $A+B_2 \rightarrow AB+B$ can be driven coherently and efficiently with quantum-degenerate bosonic or fermionic matter waves. We show that the initial stages of the reaction are dominated by quantum fluctuations, resulting in the appearance of macroscopic non-classical correlations in the final atomic and molecular fields. The dynamics associated with the creation of bosonic and of fermionic dimer-atom pairs are also compared. This study opens up a promising new regime of quantum degenerate matter-wave chemistry.

I. INTRODUCTION

The making and probing of ultracold molecular gases have attracted much attention in recent years [1], as their realization opens up exciting applications in fields ranging from condensed matter physics to quantum information science. The application of magnetic Feshbach resonances (FR) [2, 3, 4, 5, 6] and of optical photoassociation (PA) [7, 8, 9, 10], oftentimes in combination, within an atomic Bose-Einstein condensate can result in the creation of diatomic [11] as well as of more complex molecules, as evidenced by recent experimental observations of transient Efimov trimer states Cs_3 [12] and of the molecular tetramer Cs_4 (indirectly via resonances in inelastic processes) [13, 14]. We also mention the important work of Ling *et al.* [15, 16, 17], who proposed to use a chirped coupling field to compensate the effects of nonlinear collisions within the stimulated Raman adiabatic passage (STIRAP) technique [20, 21, 22, 23, 24? ?] and thus to efficiently generate large amounts of deeply bound ultracold molecules. This is an extension of previous developments in associative STIRAP (see, e.g. early work by Mackie and coworkers [24]), that is particularly relevant in the context of the present paper. The atom-molecule dark states involved in such a process was first realized experimentally via coherent two-color PA [25] in an early example of what is now called superchemistry [26].

Over the past ten years, ultracold matter-wave superchemistry has focused on coherent association or dissociation reactions [27, 28] between atoms and diatomic molecules. For example, Moore and Vardi [27] studied the possibility of an almost complete Bose-enhanced channel selectivity in the coherent photodissociation of bosonic triatomic ABC molecules, resulting from the interplay between Bose enhancement and competition between modes for a finite number of initial molecules. Other recent examples include work on the dependence of dissociation on the size or shape of the reaction vessel (confinement effect) [29] and the assembly of Fermi-degenerate dimers via cooperative association [30].

The present paper extends the toolbox of superchemistry to the coherent abstraction reaction (or bimolecular reactive scattering) $A + B_2 \rightarrow AB + B$, where A, B, B_2 and AB denote either bosonic or fermionic atoms or dimers. This reaction is an important benchmark system in chemical physics. Its dynamics has attracted much interest in recent studies of reactive resonance or low-energy non-Born-Oppenheimer reactivity through a cross-beam scattering method [31, 32]. A particularly noteworthy contribution is the study by Shapiro and Brumer of the coherent control of single-molecular photoassociation or bimolecular collisions through the interference of reactive pathways [33].

Extending these considerations to the case of ultracold matter waves, we show that the coherent abstraction reaction can be realized efficiently and controlled in a STIRAP photoassociation pulse sequence [10] such that the intermediate states are dark states. An important characteristic of this process is that it is triggered by quantum noise, leading to large shot-to-shot quantum fluctuations that invalidate the use of the Gross-Pitaevskii equation (GPE) in the initial stages. That equation can be used only at later times when the product reactant channels become macroscopically occupied. This is somewhat similar to a situation familiar in a number of quantum and atom optics examples such as the laser [34], optical and matter-wave superradiance [35], and molecular matter-wave amplifier [36], and is in contrast to the familiar single-molecular [10, 26, 37] combination reaction.

In realizing the collective reaction $A + B_2 \rightarrow AB + B$, the basic idea is to first create weakly bound trimers AB_2 via an entrance-channel atom-dimer FR, and then to dissociate them into a closed-channel bound dimer and atom via photodissociation. A key aspect of that scheme is that involving a trimer intermediate state allows one to exploit a coherent population trapping (CPT) state that prevents the trimer population from becoming significant throughout the conversion process. Such an atom-molecule state does *not* exist in other schemes that involve *e.g.* an intermediate two-species atomic state. Note also that this scheme, which is spe-

cific to quantum-degenerate matter waves, is different from a purely collision-induced reaction [38] and from the non-degenerate single-pair dynamics of reactive scattering [33]. As such it represents a promising advance in the on-going development of superchemistry [14, 26].

The remainder of this paper is organized as follows: Section II discusses our model and analyzes the initial stages of the coherent bimolecular reaction. The resulting quantum fluctuations determine the initial statistical properties of the mean-field evolution that takes over once the various matter-wave fields are macroscopically populated. This is discussed in Sec. III, where we numerically compute a large number of trajectories from initial classical seeds satisfying these short-time statistics. We also review how an approximate CPT dark state required for the STIRAP pulse sequence can be achieved in the presence of mean-field shifts. Section IV briefly discusses the possible conversion of bosons to fermions. Several generalizations, including the role of population imbalance, are considered in Sec. V. Finally Section VI is a summary and conclusion.
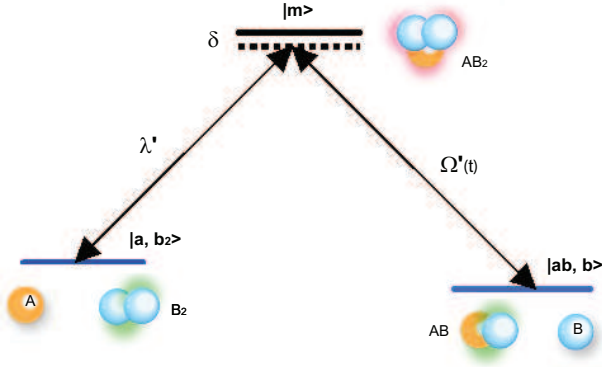
II. SHORT-TIME QUANTUM DYNAMICS

FIG. 1: (Color online) Schematics of the coherent abstraction reaction $A + B_2 \rightarrow AB + B$ with degenerate matter waves. A and B denote the bosonic or fermionic atoms, and B_2 and AB are molecular dimers.

Our model system is sketched in Fig. 1. The intermediate heteronuclear trimers AB_2 are created via FR, and then photodissociated into bound molecules AB and atoms B. Denoting the atom-dimer coupling strength with detuning δ by λ'_1, the Rabi frequency of the dissociating laser by Ω'_1 and its detuning by Δ, the dynamics of the system is described at the simplest level by the

model Hamiltonian ($\hbar = 1$)

$$
\begin{aligned}
\hat{\mathcal{H}} = -\int dr \Big\{ &\sum_{i,j} \chi'_{i,j} \hat{\psi}_i^\dagger(r) \hat{\psi}_j^\dagger(r) \hat{\psi}_j(r) \hat{\psi}_i(r) + \delta \hat{\psi}_m^\dagger(r) \hat{\psi}_m(r) \\
+ &\lambda'[\hat{\psi}_m^\dagger(r) \hat{\psi}_a(r) \hat{\psi}_{b_2}(r) + \text{H.c.}] + (\Delta + \delta) \hat{\psi}_{ab}^\dagger(r) \hat{\psi}_{ab}(r) \\
- &\Omega'[\hat{\psi}_{ab}^\dagger(r) \hat{\psi}_b^\dagger(r) \hat{\psi}_m(r) + \text{H.c.}] \Big\}.
\end{aligned}
\tag{1}
$$

We consider first a purely bosonic system. The annihilation operators $\hat{\psi}_i(r)$, where the indices $i, j = a, b, b_2, ab, m$ stand for atoms (A and B), dimers (B_2 and AB) and trimers (AB_2), satisfy the standard bosonic commutation relations

$$[\hat{\psi}_i(r), \ \hat{\psi}_j^\dagger(r')] = \delta_{ij}\delta(r - r').$$

The terms proportional to $\chi'_{i,j} = 2\pi a_{i,j}/M_{i,j}$ describe interspecies s-wave collisions with scattering length $a_{i,j}$, $M_{i,j} = M_i M_j/(M_i + M_j)$ being the reduced mass [39].

In the mean-field approximation, $\hat{\psi}_i \rightarrow \sqrt{n}\psi_i$ where n is the initial particle density, the Heisenberg equations of motion resulting from the Hamiltonian (1) are easily shown to reduce to the form

$$
\begin{aligned}
\dot{\psi}_a &= 2i \sum_j \chi_{a,j} |\psi_j|^2 \psi_a + i\lambda \psi_{b_2}^* \psi_m, \\
\dot{\psi}_b &= 2i \sum_j \chi_{b,j} |\psi_j|^2 \psi_b - i\Omega \psi_{ab}^* \psi_m, \\
\dot{\psi}_{b_2} &= 2i \sum_j \chi_{b_2,j} |\psi_j|^2 \psi_{b_2} + i\lambda \psi_a^* \psi_m, \\
\dot{\psi}_{ab} &= 2i \sum_j \chi_{ab,j} |\psi_j|^2 \psi_{ab} - i\Omega \psi_b^* \psi_m + i(\Delta + \delta)\psi_{ab}, \\
\dot{\psi}_m &= 2i \sum_j \chi_{m,j} |\psi_j|^2 \psi_m + (i\delta - \gamma)\psi_m + i\lambda \psi_a \psi_{b_2} \\
&\quad - i\Omega \psi_b \psi_{ab}.
\end{aligned}
\tag{2}
$$

Here $\chi_{i,j} = n\chi'_{i,j}$, $\lambda = \lambda'\sqrt{n}$, $\Omega = \Omega'\sqrt{n}$, and we have introduced the phenomenological decay rate γ to account for the loss of intermediate trimers, based on the assumption that this decay dominates all other loss mechanisms such as rogue photodissociation to noncondensate modes [3, 40]. As already mentioned, our goal is to minimize that decay by using a STIRAP pulse sequence, ideally permitting the full transfer of the entrance-channel state to the closed-channel state while keeping the intermediate state unpopulated at all times.

The initial condition $\psi_b(0) = \psi_{ab}(0) = 0$ is readily seen to result in

$$\psi_b(t) = \psi_{ab}(t) = 0,$$

for all times. This indicates that the mean-field GP equations break down completely in studying the onset of this type of abstraction reaction. A similar situation has been previously encountered in a broad range of systems in quantum optics [34], but also in coupled degenerate atomic and molecular systems such as the example in the matter-wave superradiance of Bose-condensed

atoms [34, 35, 36]. As in those situations, our strategy here is to decompose the problem into an initial quantum-noise-dominated stage followed by a classical stage that arises once the product components have acquired a macroscopic population. The initial quantum evolution is treated in a linearized approach whose main purpose is to establish the statistical properties of the initial fields required for the classical stage [36].

A simple physical picture of the initial stages of the coherent abstraction reaction can be obtained when considering the limiting case where δ is the largest parameter in the system, $i\dot{\hat{\psi}}_m/\delta \approx 0$. In the collisionless limit this gives

$$\hat{\psi}_m \approx -(\lambda'/\delta)\hat{\psi}_a\hat{\psi}_{b_2} + (\Omega'/\delta)\hat{\psi}_b\hat{\psi}_{ab},$$

which amounts to adiabatically eliminating the intermediate trimer state. In this case the system is described by the effective Hamiltonian

$$\hat{\mathcal{H}}_{\text{eff}} = -(G\hat{c}_{ab}^\dagger\hat{c}_b^\dagger\hat{c}_a\hat{c}_{b_2} + h.c.) + \hat{c}_0, \qquad (3)$$

where

$$\hat{c}_0 = \omega_1\hat{c}_a^\dagger\hat{c}_a\hat{c}_{b_2}^\dagger\hat{c}_{b_2} + \omega_2\hat{c}_{ab}^\dagger\hat{c}_{ab}\hat{c}_b^\dagger\hat{c}_b, \qquad (4)$$

$$\hat{\psi}_i(r,t) = \phi_i(r)\hat{c}_i(t),$$

and the various constants are

$$G = (\lambda'\Omega'/\delta)\int dr\,\phi_{ab}^*(r)\phi_b^*(r)\phi_a(r)\phi_{b_2}(r),$$

$$\omega_1 = (\lambda'^2/\delta)\int dr\,\phi_a^*(r)\phi_a(r)\phi_{b_2}^*(r)\phi_{b_2}(r),$$

$$\omega_2 = (\Omega'^2/\delta)\int dr\,\phi_{ab}^*(r)\phi_{ab}(r)\phi_b^*(r)\phi_b(r),$$

The Hamiltonian (3), which is exactly solvable, has been considered previously in the study of a spin exchange scattering process that produces entangled bosonic pairs in a two-species, two-pseudospins Bose condensate [41].

For short enough interaction times, Eq. (3) can be further simplified by taking into account the fact that the populations of the reaction products remain small compared to the total particle numbers N_0. In this regime, we can treat the fields $\hat{\psi}_a$ and $\hat{\psi}_{b_2}$ classically, $\hat{c}_{a,b_2} \to \sqrt{N_{a,b_2}}$, and then neglect the term in Eq. (3) describing only the interactions between the modes $\hat{c}_a$ and $\hat{b}_2$. As discussed e.g. in Ref. [35], this results in the linearization of the Heisenberg equations of motion for the remaining quantized matter-wave fields $\hat{c}_{ab}$ and $\hat{c}_b$, with a noise source $\hat{f}_j^\dagger(t)$,

$$\dot{\hat{c}}_{ab,b}(t) = \hat{f}_{b,ab}^\dagger(t) = i\mathcal{G}\hat{c}_{b,ab}^\dagger(t). \qquad (5)$$

Such a result is familiar from several quantum and atom optics problems, including the optical parametric oscillator [34] and molecular dissociation (pair production)

in ultracold systems [42]. For simplicity we assume in the following that the correlations of the quantum noise operators appearing in Eq. (5) are markovian,

$$\langle\hat{f}_i^\dagger(t)\hat{f}_j(t')\rangle = 0, \quad \langle\hat{f}_i(t)\hat{f}_j^\dagger(t')\rangle = \mathcal{G}^2\delta_{ij}\delta(t-t'),$$

where $\mathcal{G} = G\sqrt{N_aN_{b_2}}$ and $i,j = ab$ or b here and in the following. It is these noise operators that trigger the non-mean-field "spontaneous" evolution of the system from initial vacuum fluctuations.

The populations of the modes $j = b, ab$ and their correlations are then

$$N_j \equiv \langle\hat{c}_j^\dagger\hat{c}_j\rangle = \sinh^2(\mathcal{G}t) \approx N_aN_{b_2}G^2t^2;$$

$$\mathcal{C}_{ab} = \mathcal{C}_b \equiv \frac{\langle\Delta\hat{N}_{ab}\Delta\hat{N}_b\rangle}{\sqrt{N_{ab}N_b}} = 1 + \sinh^2(\mathcal{G}t) > 1, \quad (6)$$

where $\Delta\hat{N}_j \equiv \hat{N}_j - \langle\hat{N}_j\rangle$. Eq. (5) can also be derived by solving Eq. (3) to second order in time t with the depletions $N_{a,b_2} = N_0 - N_{ab,b}$. It is also straightforward to find that

$$\langle\hat{N}_{ab}^2\rangle = \langle\hat{N}_b^2\rangle = \langle\hat{N}_{ab}\hat{N}_b\rangle = \sinh^2(\mathcal{G}t)\cosh^2(2\mathcal{G}t)$$

and that

$$g_b^{(2)} = g_{ab}^{(2)} = \frac{\langle\hat{c}_{ab}^\dagger\hat{c}_{ab}^\dagger\hat{c}_{ab}\hat{c}_{ab}\rangle}{\langle\hat{N}_{ab}\rangle^2} = 2. \qquad (7)$$

It follows that the Mandel Q parameters [34] is given by

$$Q_{ab,b} = \frac{\langle\hat{N}_{ab,b}^2\rangle - \hat{N}_{ab,b}^2}{\hat{N}_{ab,b}} = \cosh^2(\mathcal{G}t) > 1, \qquad (8)$$

and exhibits super-Poisson statistics [34]. It is interesting to observe that although the second factorial moments of the single modes ab and b are typical of chaotic fields, quantum entanglement within these two modes does exist, i.e.,

$$g_{ab,b}^{(2)} = \frac{\langle\hat{N}_{ab}\hat{N}_b\rangle}{N_{ab}N_b} = 1 + \frac{\cosh^2(\mathcal{G}t)}{\sinh^2(\mathcal{G}t)}, \qquad (9)$$

$$\left[g_{ab,b}^{(2)}\right]^2 - g_{ab}^{(2)}g_b^{(2)} = \sinh^{-4}(\mathcal{G}t) + 4\sinh^{-2}(\mathcal{G}t) > 0,$$

violating the classical Cauchy-Schwarz inequality (CSI) [34, 43].

Similar equations of motion can be derived in case atoms A are bosonic and atoms B fermionic. The main difference in that case is in the commutation relations of the noise operators $(-\hat{f}_b^\dagger, \hat{f}_{ab}^\dagger)$. The Heisenberg equations of motion can be solved via a Bogoliubov transformation. One finds that the vacuum-noise-triggered populations of principal modes are then [42]

$$N_{ab,b} = \sin^2(\mathcal{G}t) < 1,$$

a direct consequence of the Fermi statistics [42]. Being similar to the bosonic case, we also find $\langle\hat{N}_{ab}^2\rangle = \langle\hat{N}_b^2\rangle =$

$$\sin^4(\mathcal{G}t) + \cos^2(\mathcal{G}t)\sin^2(\mathcal{G}t) = \sin^2(\mathcal{G}t), \quad \langle\hat{N}_{ab}\hat{N}_b\rangle = -\sin^2(\mathcal{G}t)\cos(2\mathcal{G}t)), \text{ and}$$

$$g_{ab}^{(2)} = g_b^{(2)} = \frac{\langle\hat{c}_{ab}^\dagger\hat{c}_{ab}^\dagger\hat{c}_{ab}\hat{c}_{ab}\rangle}{\langle\hat{N}_{ab}\rangle^2} = 0,$$

$$g_{ab,b}^2 = \frac{\langle\hat{N}_{ab}\hat{N}_b\rangle}{N_{ab}N_b} = 1 - \frac{\cos^2(\mathcal{G}t)}{\sin^2(\mathcal{G}t)},$$

$$\left[g_{ab,b}^{(2)}\right]^2 - g_{ab}^{(2)}g_b^{(2)} = [1 - \frac{\cos^2(\mathcal{G}t)}{\sin^2(\mathcal{G}t)}]^2 > 0. \quad (10)$$

The fermionic dimer-atom pairs correlations are of course also different from the bosonic case, specifically we have now $C_{ab,b} = 1 - N_{ab,b} < 1$, a signature of antibunching. Additionally, the Mandel Q parameter for the principal mode is

$$Q_{ab,b} = \frac{\langle\hat{N}_{ab,b}^2\rangle - \hat{N}_{ab,b}^2}{\hat{N}_{ab,b}} = \cos^2(\mathcal{G}t) < 1, \quad (11)$$

characteristic of subpoissonian statistics.

III. LONG-TIME CLASSICAL EVOLUTION

The long-time statistical properties of the AB and B populations, which are significantly influenced by the initial vacuum fluctuations, can be calculated by a positive-P representation technique [26] and other methods [41]. Rather than adopting such a full quantum treatment, we proceed in the following by solving the mean-field description of Eqs. (2) with stochastic classical seeds whose statistics are consistent with the results of the linearized, short-time quantum analysis [36]. To be specific, using Eqs. (2) we compute 300 trajectories with randomly chosen initial classical seeds satisfying the short-time behavior of Eq. (5).

Figure 2 shows the standard derivations $\Delta N_i(t)$ around the average values of the particle populations,

$$\Delta N_i(t) = \left\{\frac{1}{300}\sum_{n=1}^{300}\left[(N_{i,n}(t) - \bar{N}_i(t)\right]^2\right\}^{1/2},$$

with $\bar{N}_i(t) = (1/300)\sum_n N_{i,n}(t)$, for $\delta = 3$ and $\delta = -3$. The inset shows the fluctuating range $\pm\Delta N_i$ about the mean populations, $\bar{N}_i \pm \Delta N_i(t)$ for $\delta = 3$ and for bosonic atoms. The small seeds resulting from the initial quantum fluctuations are significantly amplified, increasing more rapidly than their deviations, before reaching a stationary value. For $\delta = -3$, however, no stable reaction is observed.

An important feature of the coherent abstraction reaction is that it can be controlled and optimized by exploiting the existence of a CPT dark state [25, 37]. This technique is well known in the case of linear systems, where it permits the transfer of population from an initial to a final state via an intermediate state that remains unpopulated at all times. This is the basis for stimulated
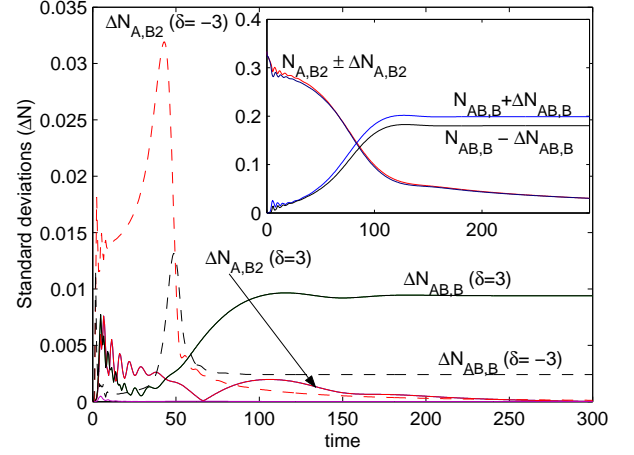

FIG. 2: (Color online) Standard derivation of the dimer and atomic populations from their average values for $\delta = 3$ and $\delta = -3$. Time is in units of λ^{-1}, and $\gamma = 1$. The other parameters are given in the text. The trimer population remains essentially zero at all times due to the CPT condition. Inset: fluctuating range of the populations $\bar{N}_i(t) \pm \Delta N_i(t)$ for $\delta = 3$.

Raman adiabatic passage (STIRAP), which achieves this goal via a so-called counter-intuitive sequence of pulses [25, 44, 45, 46].

CPT and STIRAP rely explicitly on the validity of the adiabatic theorem, which applies only to linear systems. While there have been many previous developments in associative STIRAP (see e.g. Ref. [26]), it is not immediately obvious that STIRAP still works in the usual way with a well-defined nonlinear adiabatic condition for the nonlinear system at hand, even in the collisionless limit. This question was recently investigated by Pu and coworkers in Ref. [16] for a model of coherent atom-dimer conversion, and an approximate adiabatic condition was obtained by linearizing the nonlinear system around the intended adiabatic evolution. In that context, the analytical form of the nonlinear adiabatic condition derived in the collisionless limit turns out to be useful in determining the required laser parameters [16, 17, 18, 19].

We show in the following that an approximate atom-molecule CPT state can also be achieved in the present situation. Specifically, Eqs. (2) admit a steady-state CPT solution with a trimer state that remains unpopulated at all times under the generalized "two-photon" resonance condition

$$\Delta = -\delta + (2\chi_{aa} + 6\chi_{ab} + 5\chi_{bb_2} + 2\chi_{bb})N_{b_2,s} + (2\chi_{ab} + \chi_{bb_2})N_{ab,s}, \quad (12)$$

To this end, we apply the steady-state ansatz

$$\psi_{a,s} = |\psi_{a,s}|e^{i\theta_a}e^{i\mu_a t}, \quad \psi_{b,s} = |\psi_{b,s}|e^{i\theta_b}e^{i\mu_b t},$$
$$\psi_{b_2,s} = |\psi_{b_2,s}|e^{2i\theta_b}e^{2i\mu_b t},$$
$$\psi_{ab,s} = |\psi_{ab,s}|e^{i(\theta_a+\theta_b)}e^{i(\mu_a+\mu_b)t},$$
$$\psi_{m,s} = |\psi_{m,s}|e^{i(\theta_a+2\theta_b)}e^{i(\mu_a+2\mu_b)t}, \quad (13)$$

$\mathcal{R}$	$N_{g_2,s;b,s}$	$N_{g_1,s}$	$N_{a,s}$
1	$\dfrac{1}{3+\Omega_{eff}}$	$\dfrac{2\Omega^2/\lambda^2}{(3+\Omega_{eff})(1+\Omega_{eff})}$	$\dfrac{1+\Omega_{eff}+4\Omega^2/\lambda^2}{(3+\Omega_{eff})(1+\Omega_{eff})}$
$\frac{1}{2}$	$\dfrac{1}{3(1+\Omega/\lambda)}$	$\dfrac{\Omega/\lambda}{3(1+\Omega/\lambda)}$	$\dfrac{\Omega/\lambda}{3(1+\Omega/\lambda)}$
$\frac{1}{4}$	$\dfrac{4}{5(3+\Omega_{eff})}$	$\dfrac{2(1+\Omega_{eff})}{5(3+\Omega_{eff})}$	$\dfrac{8\Omega^2/\lambda^2}{5(3+\Omega_{eff})(1+\Omega_{eff})}$

TABLE I: Steady-state CPT particle numbers, with $\Omega_{eff} = \sqrt{1+8\Omega^2/\lambda^2}$.

where μ_a and μ_b are the atomic chemical potentials. Inserting these trial functions into Eqs. (2) and taking $|\psi_{m,s}| = 0$, one finds the steady-state relation

$$\lambda\psi_{a,s}\psi_{b_2,s} = \Omega\psi_{b,s}\psi_{ab,s},$$

which, together with the condition of conserved particle numbers $N_{a,s} + 2(N_{b_2,s} + N_{ab,s}) + N_{b,s} = 1$, gives

$$\left[(\frac{\Omega}{\lambda}) - 1\right]N_{ab,s}^2 + \frac{2\mathcal{R}+1}{2\mathcal{R}+2}N_{ab,s} - \frac{\mathcal{R}}{2(\mathcal{R}+1)} = 0, \quad (14)$$

where

$$\mathcal{R} \equiv \frac{N_a(0)}{2N_{b_2}(0)} = \frac{N_{a,s}+N_{ab,s}}{N_{b,s}+N_{ab,s}+2N_{b_2,s}}. \quad (15)$$

The CPT solution is therefore

$$N_{ab,b}^s = \frac{2\mathcal{R}}{(1+\mathcal{R})\left[1+2\mathcal{R}+\sqrt{(1-2\mathcal{R})^2+8\mathcal{R}\Omega^2/\lambda^2}\right]}.$$

Table 1 displays the CPT particle numbers for several values of $\mathcal{R}$. Note that from the conservation of particle numbers we have $N_{b,s} = N_{ab,s}$ and

$$N_{b_2,s} = \frac{1}{2(1+\mathcal{R})} - N_{ab,s}.$$

In addition, we note that an initial populations imbalance can also significantly affect the dynamics of atom-molecule conversion for our present bimolecular reactions. The condition $\partial N_{ab,s}/\partial\mathcal{R} = 0$ yields a maximum dimer number

$$N_{ab,s}|_{\max} = 1/3,$$

corresponding to a complete abstraction reaction for $\mathcal{R} = 1/2$ or the so-called "balanced case". We consider this case first and then turn to study the effect of initial populations imbalance (see Section V).

We have numerically solved Eqs. (2) and the typical results are showed in Fig. 3. In this specific example atom A is ^{87}Rb, atom B is ^{41}K, $\lambda = 4.718 \times 10^4 \text{s}^{-1}$ and

$$\Omega(t) = \Omega_0\text{sech}(t/\tau),$$

with $\Omega_0/\lambda = 20$ and $\lambda\tau=20$ [50]. The collision parameters, in units of λ/n, are $\chi_{aa} = 0.5303$, $\chi_{bb} = 0.3214$, $\chi_{ab} = 0.8731$, all others being equal to 0.0938 [50]. As mentioned earlier, we have neglected rogue photodissociation to noncondensate modes, which is proved through

our direct calculations to be a safe approximation for the present parameters of our model [51, 52, 53]. On the other hand, we note that the scattering lengths of the various particles collisions, especially those involving molecular dimers or even some trimers, depend on the details of the interatomic potential, are yet not known. However, in our numerical calculations it is straightforward to use a large set of plausible collision parameters for the Rb-K, Rb-Na or other alkali atomic samples. We actually have done this and found essentially the similar result as Fig. 3: stable bimolecular conversion is always possible for appropriate values of the external field detuning δ, which is independent of the precise collision values. This result finds its origin in the underlying mechanism of "generalized STIRAP,' first proposed by Ling et al. [15] in the context of atom-dimer conversion, and according to which collisions need not limit the conversion rate as long as one chooses an adiabatic passage route that compensates for the collisional mean-field phase shifts (see Eq. (12)).

Figure 3 shows the creation of AB and B for $\delta = \pm3$ and $\delta = \pm1$. The results are essentially the same as those of Ref. [37] for $\delta = \pm3$. For this bosonic system, stable bimolecular conversion is always possible for negative detunings, but the system can be unstable for positive detunings (see Fig. 3). The increasing departure of the product populations from the ideal CPT line is due to the fact that only an approximate adiabatic condition exists for the CPT state.

We also analytically derived the adiabaticity parameter introduced by Pu et al. in the collisionless limit [16, 54],

$$\gamma_{\text{nl}}(t) \approx \frac{|\dot{\eta}|}{1+\eta}\frac{1}{4\lambda} \ll 1,$$

where $\eta = \lambda/\Omega$. This expression differs from that for the corresponding linear system [16] in that in the latter case η is replaced by η^2 in the denominator. Hence adiabaticity becomes increasingly difficult to maintain in the final stages of the STIRAP process, similarly to the case of atom-dimer conversion [16].

We remark that this scheme relies crucially on the capability to avoid rapid collisional quenching or the formation of an unstable atom-dimer sample. When energetically allowed, collision-induced reactions always occur at some rate, and we need to guarantee that the time scale over which quantum fluctuations dominate the dynamics is short enough, so that the dynamics of the system is not collision-dominated.

In order to estimate the upper limit on collisions, we can use the condition $|\mathcal{G}t| < 1$ or

$$|G\sqrt{N_aN_{b_2}}t| < 1,$$

which determines the validity of the short-time approximation for the early quantum stage, to estimate the time over which the fluctuations take place. This upper time limit is of the order of 10^{-5}s for $|\delta = 3|$ and
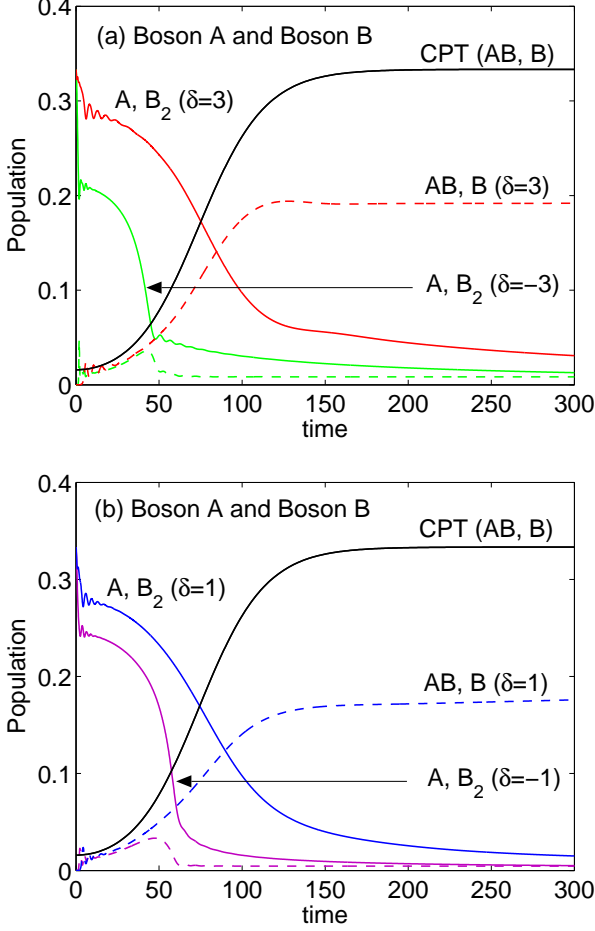
FIG. 3: (Color online) Populations of the bosonic dimers and atoms for (a) $\delta = \pm 3$ or (b) $\delta = \pm 1$. Time is in units of λ^{-1}, and $\gamma = 1$. The line labelled "CPT" shows the ideal population of products (dimers AB and atoms B).

$\Omega_0 = 20\lambda$. According to Cvitas *et al.* [55], typical low-temperature inelastic collision cross-sections are of the order of $10^{-17} m^3/s$, corresponding to reaction times of the order of $10^{-3}s$ for a typical condensate density of $10^{14} cm^{-3}$. From that estimate, it appears that the fluctuations do indeed dominate for short enough times. We also note that the collisional reaction time of 10^{-3}s corresponds to an almost complete noise-amplified conversion in Fig. 3. In that case the fluctuation-induced dynamics completely dominate the short-time behavior of the system. This feature, which is characteristic of a wide variety of collective abstraction reactions, may provide a useful means to produce reaction products that are difficult to obtain or have only poor yield when resulting from a purely collisional method.

IV. BOSONS TO FERMIONS CONVERSION

When considering a mixture of bosonic and fermionic atoms, the abstraction reaction results in the conversion of bosonic to fermionic molecules,

$$\mathbf{b} + \mathcal{B} \to \mathcal{F} + \mathbf{f},$$
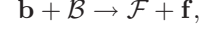
where $\mathbf{b}$ $(\mathcal{B})$ or $\mathbf{f}$ $(\mathcal{F})$ denotes bosonic or fermionic atoms (dimers). Ignoring s-wave collisions between fermionic atoms of the same species and retaining only their dominant kinetic energy, and assuming further that collisions are the dominating term for the bosons [56], the Hartree energy density of the system is

$$
\begin{aligned}
E =\ & \sum_{i \neq j} \chi'_{i,j}|\psi_i|^2|\psi_j|^2 + \delta|\psi_d|^2 + (\Delta+\delta)|\psi_{ab}|^2 \\
& + \lambda'\big[\psi_d^*\psi_a\psi_{b_2} + h.c.\big] - \Omega'\big[\psi_{ab}^*\psi_b^*\psi_d + h.c\big] \\
& + \sum_{i=(a,b_2,d)} \frac{1}{2}\chi'_i|\psi_i|^4 + \sum_{f=(ab,b)} \frac{3}{5}A'_f|\psi_f|^{10/3}. \quad (16)
\end{aligned}
$$

Here the indices i, j have the same meaning as in Eq. (1) and $A'_f = (6\pi^2)^{2/3}/2M_f$, where M_f $(f = ab, b)$ is the mass of the fermionic components.

Due to the fermionic components of the reaction partners, the ordinary mean-field approach [57, 58] adopted in studying systems with large numbers of condensed bosonic particles is inadequate here. We follow instead the approach of Ref. [56], starting from the mean-field Lagrangian density of the system

$$\mathcal{L} = \frac{i}{2}\sum_i \Big(\psi_i^*\frac{\partial\psi_i}{\partial t} - \psi_i\frac{\partial\psi_i^*}{\partial t}\Big) - E \quad (17)$$

and exploiting the Euler-Lagrange equations

$$\frac{\partial\mathcal{L}}{\partial\psi_i^*} - \partial_\mu\Big(\frac{\partial\mathcal{L}}{\partial(\partial_\mu\psi_i^*)}\Big) = 0. \quad (18)$$

to derive the mean-field dynamical equations

$$
\begin{aligned}
\dot\psi_a =\ & 2i\sum_j \chi_{a,j}|\psi_j|^2\psi_a + i\lambda\psi_{b_2}^*\psi_d; \\
\dot\psi_b =\ & 2i\sum_{j\neq b} \chi_{b,j}|\psi_j|^2\psi_b + iA_b|\psi_b|^{4/3}\psi_b - i\Omega\psi_{ab}^*\psi_d, \\
\dot\psi_{b_2} =\ & 2i\sum_j \chi_{b_2,j}|\psi_j|^2\psi_{b_2} + i\lambda\psi_a^*\psi_d \\
\dot\psi_{ab} =\ & 2i\sum_{j\neq ab} \chi_{ab,j}|\psi_j|^2\psi_{ab} + iA_{ab}|\psi_{ab}|^{4/3}\psi_{ab} \\
& - i\Omega\psi_b^*\psi_d + i(\Delta+\delta)\psi_{ab}, \\
\dot\psi_d =\ & 2i\sum_j \chi_{d,j}|\psi_j|^2\psi_m + (i\delta - \gamma)\psi_m + i\lambda\psi_a\psi_{b_2}. \quad (19)
\end{aligned}
$$

These equations are similar to Eqs. (2) with the substitution

$$\chi_{j,j}|\psi_j|^2 \to A_j|\psi_j|^{4/3}, \quad (20)$$

a consequence of the fact that we consider only the dominating kinetic energy term ignore s-wave collisions between identical fermionic particles [56].

In the CPT regime, the steady-state number of fermionic species AB and B is therefore in the same form as in the purely bosonic case, see Table I. However, the generalized "two-photon" resonance condition is now written as

$$\Delta = -\delta + 2(\chi_{ab} + \chi_{aa} + \chi_{ab_2})N_{b_2,s} + 4\chi_{ab}N_{ab,s}$$
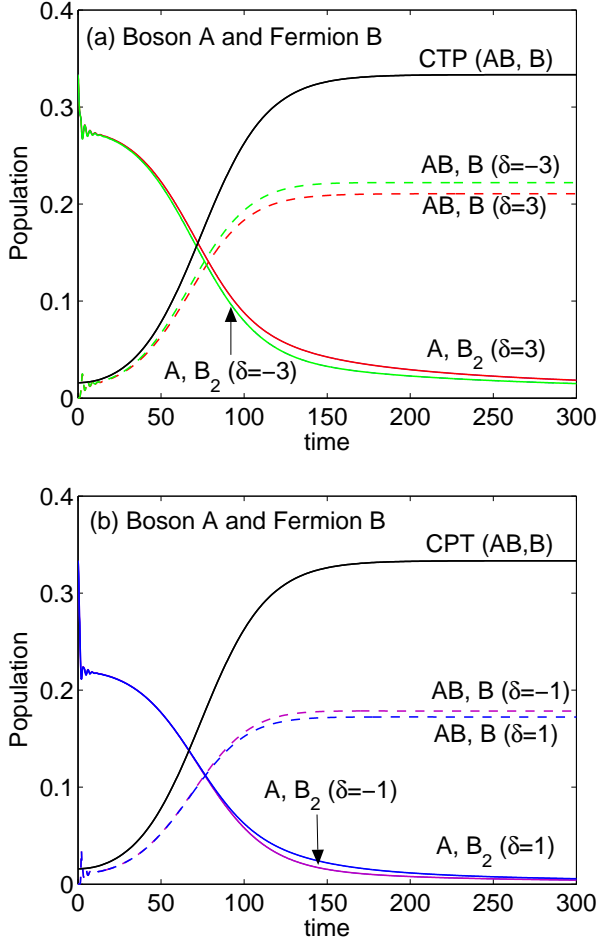$$+ (A_b - A_{ab})N_{ab,s}^{2/3}. \tag{21}$$

FIG. 4: (Color online) The generation of fermionic dimers AB and atoms B for (a) $\delta = \pm 3$ or (b) $\delta = \pm 1$ initially with no particle populations imbalance. The CPT values of the dimer AB and atomic B are also plotted.

Our numerical simulations of this case are summarized in Fig. 4 for the collision parameters $\chi_{aa} = 0.5303$, $\chi_{bb} = 0$, $\chi_{ab} = \chi_{b,ab} = \chi_{a,ab} = -0.09$, $\chi_{a,ab} = -0.2637$, $A_b = 0.008$, $A_{ab} = 0.004$, and all other collision parameters equal to zero. These results show that the stable formation of dimers AB is possible for both positive and negative detunings ((a)$\delta = \pm 3$ or (b)$\delta = \pm 1$), initially with no particle populations imbalance.

We note that in contrast to the purely bosonic case, the creation of fermion-fermion pairs is due to a statistics-independent cooperating many-body effect that has been previously recognized in the case of, e.g., matter-wave four-wave mixing [59]. We also note that in recent work Li *et al.* [60] used a similar atom-molecule dark-state technique to realize a so-called laser-catalyzed bimolecular reaction (or the conversion of fermionic to bosonic molecules):

$$^{6}\text{Li} + ^{6}\text{Li}^{7}\text{Li} \rightarrow ^{6}\text{Li}_2 + ^{7}\text{Li},$$
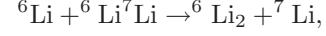
with an ultrahigh conversion rate of 99.97% [60].

V. ROLE OF POPULATION IMBALANCE

Population imbalance often plays an important role in the physics of ultracold matter waves. For example, using a two-spin-state mixture of ultracold fermionic atoms, population imbalance can induce a superfluid to normal phase transition [61]. In the following we demonstrate that an initial population imbalance can also significantly affect the dynamics of this coherent collective abstraction reaction. To this end we plot the conversion rate as a function of $\mathcal{R}$, see Eq. (14). Section III showed that in the collisionless limit $N_{ab,s}$ reaches its maximum for $\mathcal{R} = 0.5$. This value is modified slightly when taking into account of the particle collisions and the decay rate γ in our numerical simulations.

In Fig. 5, we see that the conversion rate $|\psi_{ab}(t = \infty)|^2$ now has the maximum at the value somewhat larger than $R = 0.5$ for the both bosonic and fermionic cases. In addition, we observe that the initial population imbalance has different effects for bosons and for fermions: for bosonic atoms A and B, the final conversion rates can be changed quite sharply with $\mathcal{R}$ and rapidly approach zero for $\mathcal{R} < 0.4$ and $\mathcal{R} > 1.4$; in contrast, for the case of fermionic atoms B, the conversion rate changes its shape more slowly with $\mathcal{R}$ (even for $\mathcal{R} > 1.4$, the occupation of the product species is still in excess of 7%).

Finally, we remark that we can follow a similar approach to study the collective multi-molecular reactions $2AB \rightarrow A_2 + B_2$ and $2A_2 \rightarrow A_3 + A$. In the first case we find that the steady-state CPT values of the product dimer A_2 or B_2 are the same as that of AB in the $A + B_2 \rightarrow AB + B$ reaction for $\mathcal{R}=1/2$, see Table I. For the reaction $2A_2 \rightarrow A_3 + A$, we obtain the equations of
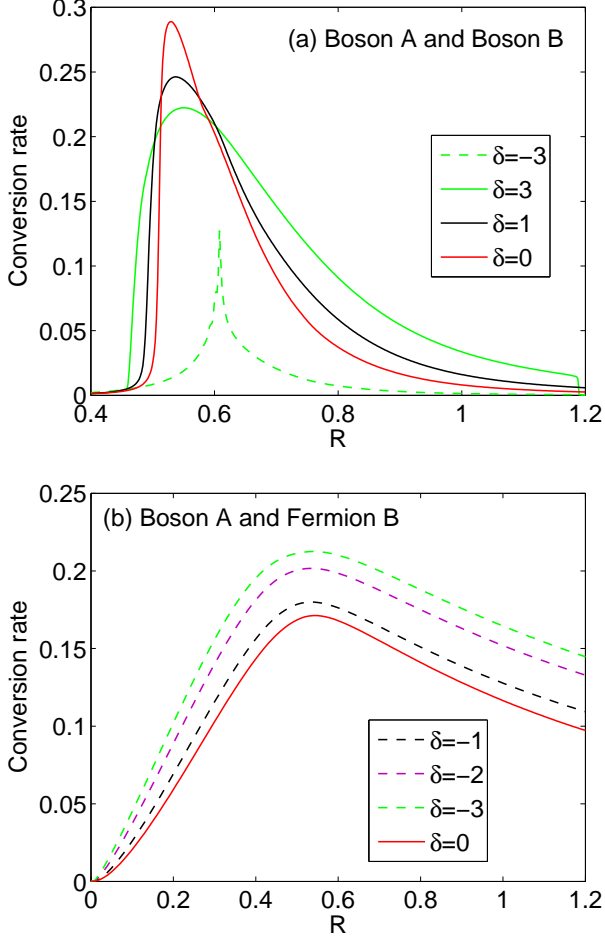
tion as

$$N^s_{a_3,a} = \frac{1}{2(2+\Omega/\lambda)}. \tag{24}$$

We have carried out numerical simulations for this case and found results similar to those sumarized in Fig. 3.

VI. CONCLUSION

In conclusion, we have shown that in quantum-degenerate ultracold atomic and molecular systems the abstraction reaction $A + B_2 \rightarrow AB + B$ can be fundamentally different from the familiar atom-molecule combination. The quantum noise that triggers this reaction leads to the creation of strongly correlated dimer-atom pairs [41]. In addition, a generalized atom-molecule dark state existing in this system can significantly enhance the creation of boson-boson or fermi-fermi dimer-atom pairs. Our study opens up a new direction in association resonances and thus a fascinating new regime of superchemistry. In particular it can be generalized to the analysis of more multi-molecular matter-wave reactions, such as the reaction $2AB \rightarrow A_2 + B_2$ or the creation of a quantum-entangled atom-molecule laser $A + A + A \rightarrow A + A_2$ [12, 39, 62], controlled even by purely optical means.

Future work will investigate the unique "superchemistry" effects of ultra-selectivity or confinement-induced stability on the bimolecular reactions, the collective abstraction reaction in a double-well potential or an optical lattice, and the possible applications of these kinds of reactions in realizing laser-catalyzed atomic spin mixing in a spinor-1 Bose condensate [27, 63]. In addition, a complete analysis of collisional effects [38, 64] will be considered. While experiments along the line of this analysis promise to be challenging, recent progress in quantum degenerate chemistry [15, 25, 27] and in the manipulation of atom-molecule systems [12, 14, 60, 65, 66, 67] indicates that achieving this goal should become possible in the not too distant future.

FIG. 5: (Color online) Final dimer population $|\psi_{ab}(t=\infty)|^2$ as the function of R for (a) the Bose case and (b) the Fermi case for several values of δ.

motion

$$\dot{\psi}_a = 2i \sum_j \chi_{a,j} |\psi_j|^2 \psi_a - i\Omega \psi^*_{a_3} \psi_t;$$

$$\dot{\psi}_{a_2} = 2i \sum_j \chi_{a_2,j} |\psi_j|^2 \psi_{a_2} + 2i\lambda \psi^*_{a_2} \psi_t;$$

$$\dot{\psi}_{a_3} = 2i \sum_j \chi_{a_3,j} |\psi_j|^2 \psi_{a_3} + i(\Delta+\delta)\psi_{a_3} - i\Omega \psi^*_a \psi_t,$$

$$\dot{\psi}_t = 2i \sum_j \chi_{t,j} |\psi_j|^2 \psi_t + (i\delta-\gamma)\psi_t + i\lambda \psi_{a_2}\psi_{a_2}$$
$$- i\Omega \psi_{a_3}\psi_a, \tag{22}$$

from which it is straightforward to show that the "two-photon" resonance condition is

$$\Delta = -\delta + (3\chi_{a_2,a} - 2\chi_{a_t,a})|\psi^s_a|^2 + (3\chi_{a_2,a_2} - 2\chi_{t,a_2})|\psi^s_{a_2}|^2$$
$$+ (3\chi_{a_2,a_3} - 2\chi_{t,a_3})|\psi^s_{a_3}|^2. \tag{23}$$

Introducing a steady-state ansatz similar to Eqs. (12), we can then calculate the CPT value of the trimer popula-

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